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## 13. ABSTRACT (Maximum 200 words)

The effect of the addition of  $ZrO_2$  to  $Li_2O-Al_2O_3-SiO_2$  glass-ceramics has been investigated. Specifically, the influences of the amount of  $ZrO_2$  added and the crystalline phase of the precipitated  $ZrO_2$  on fracture toughness were investigated. Upon heat-treatment, metastable tetragonal  $ZrO_2$  was found to precipitate in the glass-ceramics. It was found that the fracture toughness of the resulting glass-ceramics increased with increasing amounts of  $ZrO_2$  added, while that of the corresponding glasses were nearly independent of the  $ZrO_2$  content.

With a constant zirconia content, the metastable tetragonal zirconia increased in size and transformed spontaneously to stable monoclinic zirconia with a prolonged heat-treatment. Fracture toughness of the resulting glass-ceramics was found to increase steadily with the increasing fraction of monoclinic zirconia, contrary to the trend expected from the conventional toughening model. It was suggested that the strong stress field around the transformed zirconia particles are causing crack deflection, increasing the fracture toughness. Scanning electron microscope observation of the fracture surface appears to confirm this model.

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**HIGH-TOUGHNESS GLASS-CERAMICS**

**Final Report**

**Minoru Tomozawa**

**April 10, 1991**

**U.S. Army Research Office**

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## I. Statement of the Problem Studied

It is known that metastable tetragonal zirconia incorporated in a ceramic material can increase its fracture toughness<sup>1</sup>. A similar toughening was also realized for glass-ceramics in which tetragonal zirconia was precipitated<sup>2,3</sup>.

Effect of  $\text{ZrO}_2$  addition to  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  glass-ceramics has been investigated. Specifically, the influences of the amount of  $\text{ZrO}_2$  added and the crystalline phase of the precipitated  $\text{ZrO}_2$  on fracture toughness of the glass-ceramics were investigated.

## II. Summary of the Most Important Results

It was found that the fracture toughness of the resulting glass-ceramics increased with increasing amount of added  $\text{ZrO}_2$  while that of the corresponding glasses was nearly independent of  $\text{ZrO}_2$  content.

For one composition,  $22.2\text{Li}_2\text{O}-18.9\text{Al}_2\text{O}_3-55.9\text{SiO}_2-3.0\text{P}_2\text{O}_5$  (wt%) containing 15 wt% zirconia, details of the relation between the zirconia phase and fracture toughness were investigated.

Glass with the above composition was melted at  $1500^\circ\text{C}$  for 4 hours and heat-treated at  $525^\circ\text{C}$  for 52 hours for crystal nucleation and at  $955^\circ\text{C}$  for various length of time for crystal growth. Within 4 hours at  $955^\circ\text{C}$  lithium silicate, lithium alumino-silicate and tetragonal zirconia phases crystallized nearly completely. The subsequent heat-treatment increased the size of zirconia particles and caused their spontaneous transformation to monoclinic zirconia. This is demonstrated in Figure 1 where the X-ray diffraction peaks of tetragonal and monoclinic zirconia are shown. The fraction of monoclinic zirconia of the total zirconia was evaluated from the

integrated intensities of these diffraction peaks<sup>4</sup> and is shown in Figure 2. This indicates that the fraction of monoclinic zirconia increases with increasing heat-treatment time at 955 °C reaching 97% after 400 hours. Average particle sizes of both tetragonal and monoclinic zirconia were evaluated from X-ray line broadening and are shown in Figure 3.

Fracture toughness of the resulting glass-ceramics was measured by both the indentation method<sup>5</sup> and the Single-Edge-Precracked-Beam (SEPB) method<sup>6</sup>. The former is simpler, requiring a smaller sample, but the latter is known to give more accurate data. Although the two methods often give different values of the fracture toughness, the trend of the measured values agree. The measured fracture toughness is shown in Figure 4 as a function of monoclinic zirconia fraction. This clearly shows that the fracture toughness increases with increasing amounts of monoclinic zirconia.

It has been proposed that the extent of the toughening increases by transformation is given by <sup>7</sup>

$$DK_{IC} = cEV_f e^T h^{\frac{1}{2}} / (1+v) \quad (1)$$

where  $c$  is constant  $<1$  which depends upon assumptions about the nature of the transformation

$E$  = Young's modulus of the matrix

$V_f$  = volume fraction of transformable zirconia

$e^T$  = transformation strain

$h$  = transformation zone height

$v$  = Poisson's ratio

This equation suggests that, with other factors kept constant, fracture toughness should increase with increasing amount of transformable, i.e. tetragonal, zirconia.

The fracture toughness of the specimens investigated here increased, contrary to the prediction of the above equation, with increasing amounts of transformed, i.e. monoclinic, zirconia. The above equation also shows that the fracture toughness increases with the square root of the transformation zone height. It has been reported<sup>8</sup> in some glass-ceramic systems that the size of this transformation zone is nearly the same as the tetragonal zirconia particles size. In the present system, even though the particle size of tetragonal zirconia is increasing, from 300 Å to 500 Å by increasing the heat-treatment time from 4 to 400 hours, this does not seem to be sufficient to account for the observed increase of the fracture toughness. Furthermore, after 400 hours at 955 °C, the remaining amount of tetragonal zirconia is negligibly small, approximately 3%, and it is unlikely that this small quantity of tetragonal zirconia is causing the appreciable toughness increase observed.

Alternatively, we believe that the large quantity of the transformed, monoclinic zirconia and associated stress field are responsible for the toughness increase. Zirconia transformation in a rigid glass-ceramic matrix is accompanied by a large stress field and this can cause crack deflection and fracture toughness improvement. Scanning electron micrographs of the fracture surface shown in Figure 5 appears to support the present interpretation, indicating the greater toughness with increasing monoclinic zirconia fraction.

### III. List of Publications and Technical Reports

"Mechanical Properties of a Transformation Toughened Glass-Ceramic" G.L. Leatherman and M. Tomozawa

J. Mat. Sci., 25, 4488-4494 (1990).

Progress Report, 1 February 1989-30 June 1989 M. Tomozawa

Progress Report, 1 July 1989-31 December 1989 M. Tomozawa

Progress Report, 1 January 1990-30 June 1990 M. Tomozawa

Progress Report, 1 July 1990-30 December 1990 M. Tomozawa

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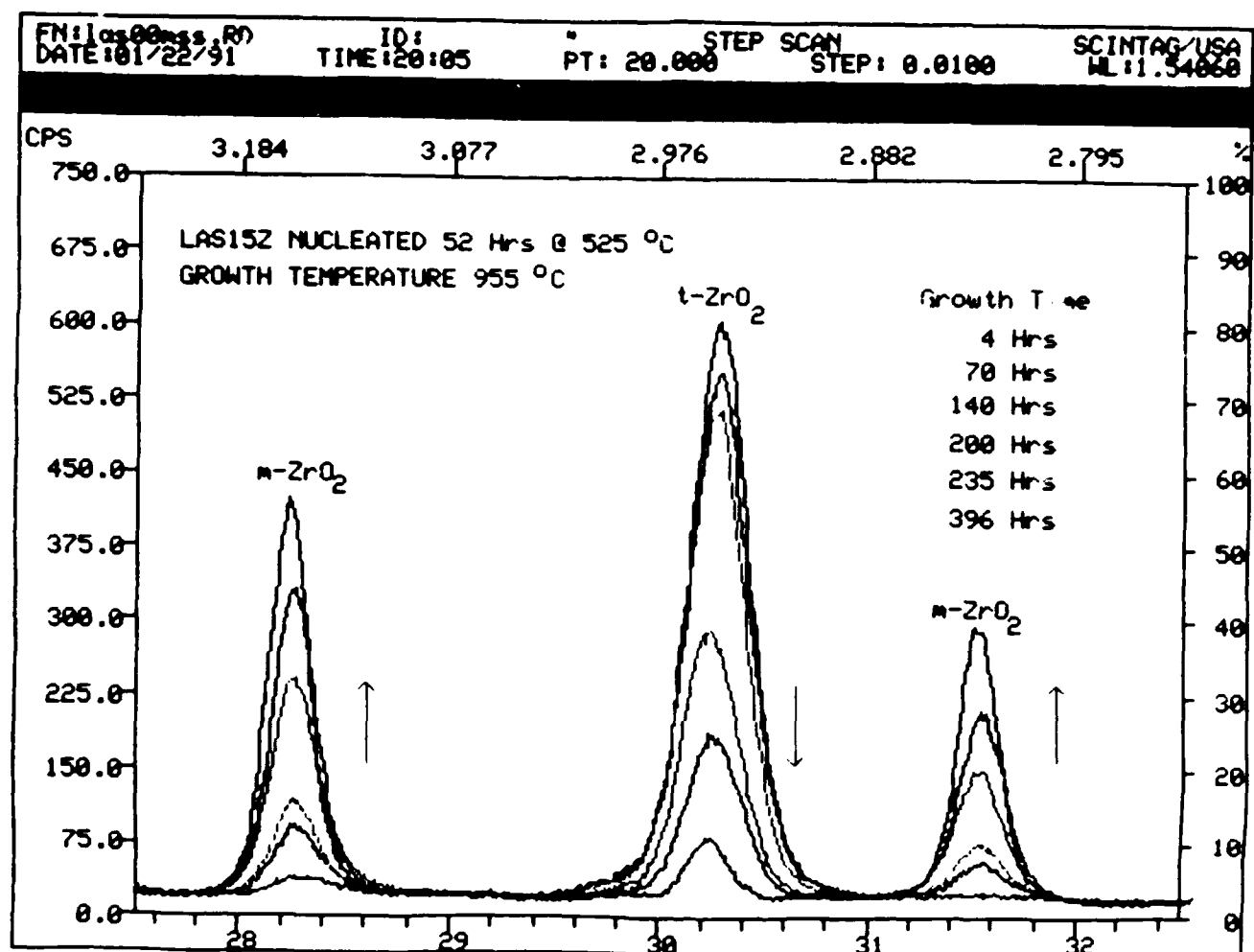


Figure 1. X-ray diffraction pattern showing the increase in monoclinic and decrease in tetragonal zirconia peaks for specimens heat-treated at 955 °C for 4 to 400 hours.

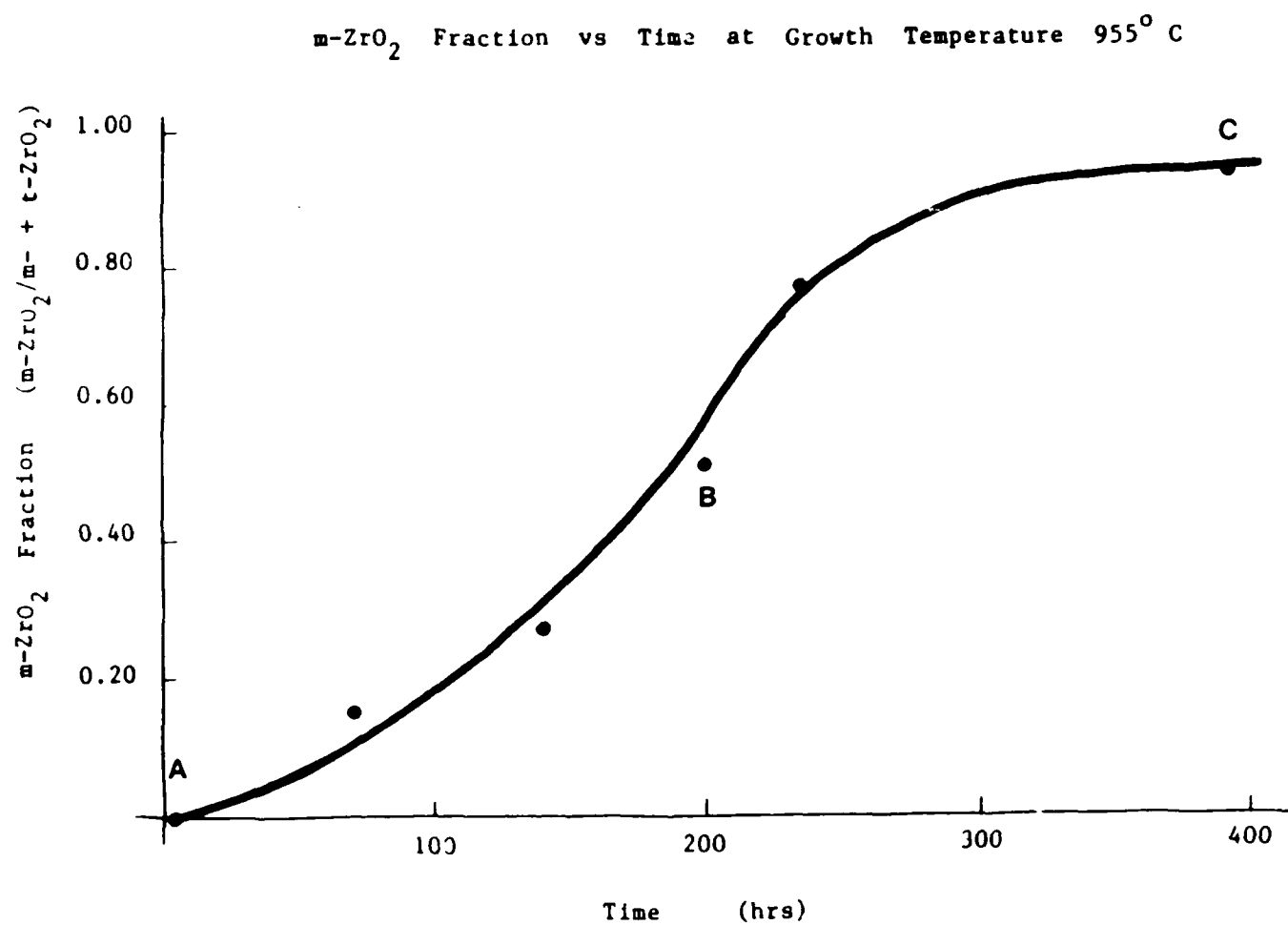


Figure 2. Volume fraction of total zirconia that is monoclinic as a function of heat-treatment time at  $955^\circ\text{C}$ . A, B, C, refer to specimens A, B, C in Figure 5.

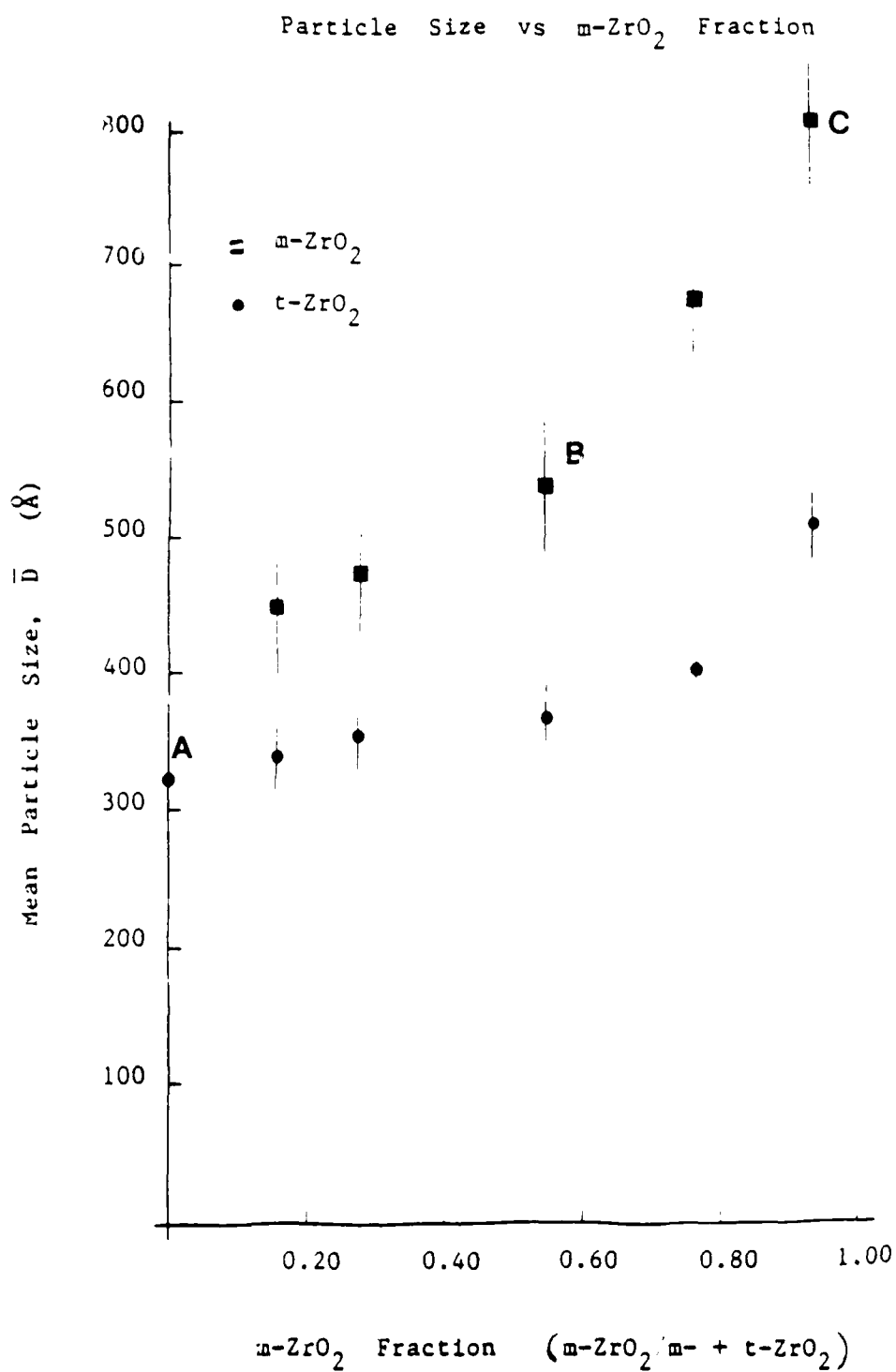


Figure 3. Mean particle size of tetragonal and monoclinic zirconia as determined by X-ray line broadening. A, B, C refer to specimens A, B, C in Figure 5.

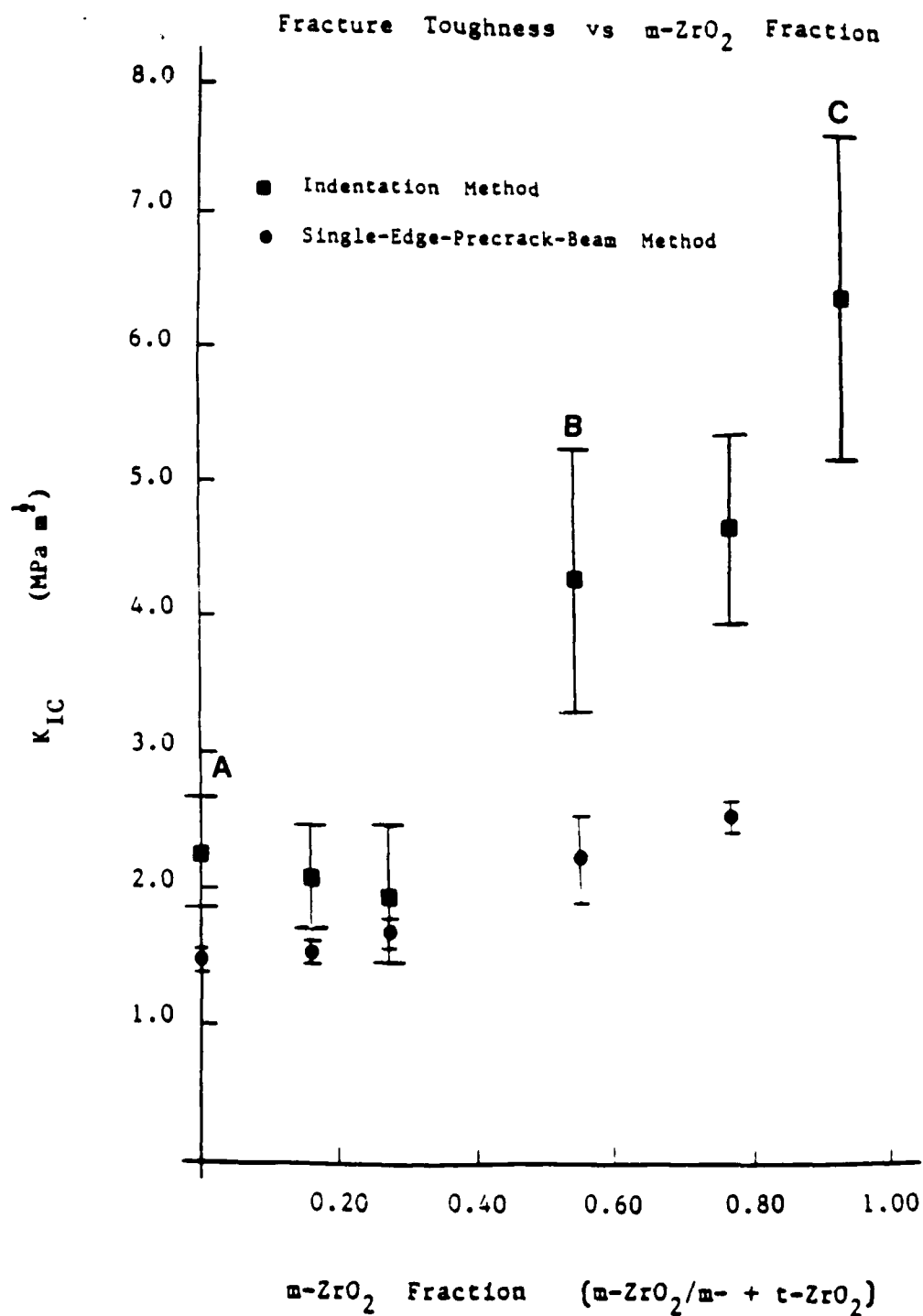


Figure 4. Fracture toughness ( $K_{IC}$ ) as measured by indentation and SEP-B methods as a function of monoclinic zirconia fraction. Both methods show an increase in toughness as the monoclinic fraction is increased. A, B, C refer to specimens A, B, C in Figure 5.

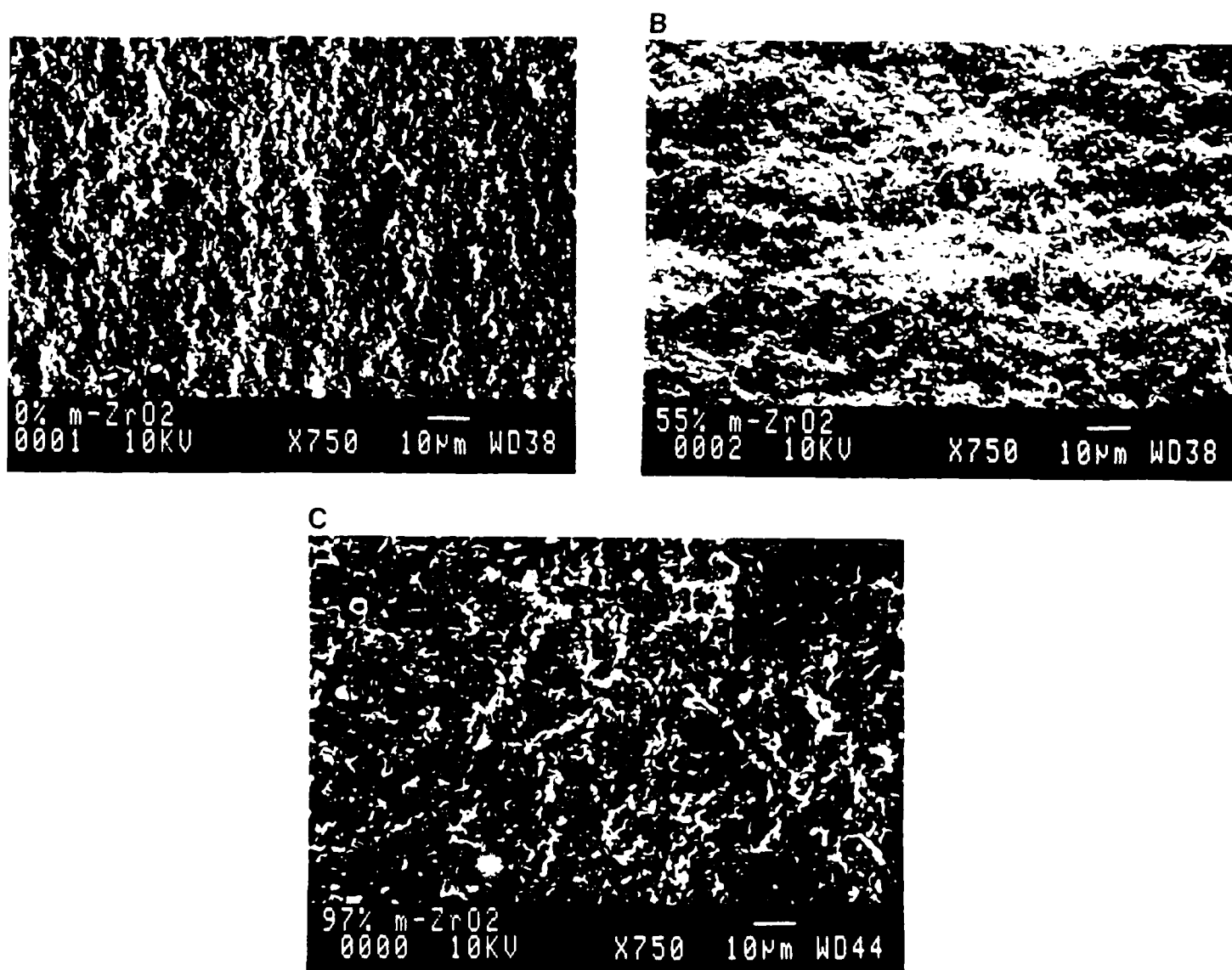


Figure 5. Scanning electron micrographs of the fracture surfaces of the (A) 0% , (B) 55% and (C) 97% monoclinic zirconia specimens at 750 X showing the increasing roughness of the surface as the monoclinic fraction is increased.